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Review

Metal–salen complexes as efficient catalysts for the oxygenation of heteroatom containing organic compounds—synthetic and mechanistic aspects

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Contents

Abstract

The metal–salen complexes (metal = Mn, Cr, Fe, Ru, Co, V and Ti) find widespread use as efficient catalysts for the selective oxygenation of organic sulfides, sulfoxides and aromatic amines. The active oxidant can be generated from the metal–salen ion using PhIO, H_2O_2, *t*-BuO_2H and ClO^- as the oxygen source. The catalytic activity of these complexes can be finely tuned by introducing substituents in the 3- and 5-positions of the salen ligand. As far as Cr(V) oxidation of amine is concerned, the addition of donor ligand is indispensable to get

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the oxygenated product. In the absence of donor ligand, oligomerization is a predominant process. Organic sulfoxides perform dual role as substrates and as donor ligand. This review summarizes recent studies on the metal–salen ion catalysed oxygenation of heteroatom containing organic compounds, in particular, those incorporating sulfur and nitrogen.

Keywords: Metal–salen complexes; Catalysis; Oxygenation; Heteroatom

1. Introduction

The selective oxygenation of organic compounds catalysed by transition metal ions is one of the most productive and elegant techniques for the oxo functionalization of organic substrates [1,2]. For this transformation to take place, the catalyst must be designed in such a way to avoid the Fenton chemistry that occurs when metal ions such as ferrous or ferric ion interact with oxidants to produce radical species [3,4]. Clearly, the metal ion should generate a type of reactive intermediate that is very reactive, but more selective than the reactive intermediates of Fenton systems. It is broadly recognized that one such possible intermediate is a terminal metal-oxo, metal-peroxo and bridging oxo complex of various types. The terminal oxo complex can arise when a single catalytic metal ion abstracts an oxygen atom from an oxygen source making two-electron oxidized metal-oxo species.

In the last decade, salen ligand [salen = 1,6-bis(2-hydroxyphenyl)-2,5-diazahexa-1,5-diene] and its derivatives have received more attention, mainly because of their extensive applications in the fields of synthesis and catalysis [5–10]. This attention is still growing, a considerable research effort is devoted to the synthesis of modified and supported reagents for catalysis and materials chemistry [11–14]. Due to the structural rigidity combined with the ease of preparation and derivatization of salen ligand, it is an attractive scaffold for the development of bifunctional complexes [14,15]. Salen ligands bind metal ions through four atoms, two nitrogen and two oxygen atoms. This tetradentate-binding motif is reminiscent of the porphyrin framework in the heme-based oxidative enzymes [16–18]. Nonetheless, salen derivatives are more easily synthesized than porphyrins and their structures are more easily manipulated to create an asymmetric environment around the active metal site. A breakthrough has been the introduction of chiral manganese–salen catalyst by the groups of Jacobsen and Katsuki, particularly, for the epoxidation of alkenes [5,6,19–22]. The Jacobsen–Katsuki reaction is universally accepted as one of the most useful and widely applicable methods for the epoxidation of unfunctionalized olefins. Chromium and cobalt complexes of the same ligand framework catalyse highly enantioselective ring opening reactions of epoxides by a variety of different nucleophiles [23,24]. Researchers anticipated that the mechanisms of epoxidation and epoxide ring opening to be similar [25]. However, subsequent investigations revealed that the catalyst functions very dissimilarly in the two processes [26,27]. In epoxidation, the catalyst serves simply as an oxo-transfer agent, whereas in epoxide ring opening, it plays a dual role, serving both as a Lewis acid to activate the epoxide and as a counterion for the nucleophile. This mechanistic insight serves as an inspiration for the development of cyclic oligomeric salen complexes that display dramatic reactivity and higher enantioselectivity relative to their monomeric counterparts [13,28].

The key problems that the studies of the catalytic reaction cycle need to address are: (a) the nature of the oxygen-transferring species; (b) the mechanism of oxygen transfer to the organic substrate; (c) the highly efficient stereochemical communication between catalyst and substrate; and (d) tuning the catalytic activity of metal–ligand system. In this respect, metal–salen complexes have several advantages and these have been outlined in recent reports [29–32].

Though many groups have extensively used these metal–salen complexes for the epoxidation reaction [5–11,19–22,29,33–39] and reasonably reviewed [5–11], employment of these catalysts for the oxidation of organic substrates containing heteroatoms like S, N and P is limited. In the past decade, our group has concentrated on the utilization of metal–salen complexes (Cr, Mn, Fe and Ru) as catalysts for the oxygenation of heteroatoms [30–32,40–44]. The important observations from our laboratory and others on the metal–salen ion catalysed oxygenation of heteroatom containing organic compounds particularly S and N are briefly reviewed in this article.

2. Active oxidizing species

An essential feature for understanding the mechanism of the oxygenation reaction is the electronic structure of the active species and how it is affected by the nature of the oxygen source, substituents in the ligand, medium of the reaction and by coordination of axial ligands. Indeed, knowledge of electronic structure of the active species is decisive for understanding the nature of the terminal M–O bond and its reactivity [45].

2.1. Iron and ruthenium

Iron plays a unique role in biological systems, as enzymes containing iron are of crucial importance in electron transfer reactions and in the activation and transport of small molecules, such as molecular oxygen [16–18,46,47]. Despite the similarity between the porphyrin and salen, so far less attention has been paid on the catalytic role of

iron(III)–salen complexes in contrast to the widespread interest in iron(III)–porphyrin catalysed oxygenation of organic substrates containing heteroatoms [1,2,16–18].

The iron(III)–salen complexes are likely to mimic the oxygenase activity of enzymes like cytochrome P-450 [48]. The oxo(salen)iron complexes generated from iron(III)–salen complexes and PhIO are characterized by UV–vis, resonance Raman (RR), EPR and ESIMS spectral techniques. The parent iron(III)–salen complex shows characteristic absorption at λ_{max} = 470 nm. The formation of oxo iron complex is inferred from the following experimental observations: (i) the dark colour of the iron(III)–salen solution fades upon the addition of PhIO; and (ii) there is a substantial decrease in the absorbance and a shift in the λ_{max} value. Resonance Raman spectra of iron(III)–salen and oxo(salen)iron complexes are recorded at room temperature using excitation at 488 nm ($ArO^- \rightarrow Fe$ CT transition). For the parent salen complex $[Fe^{III}(salen)]^+$ and its oxo complex $[O{=}Fe^{IV}(salen)]^{\bullet+}$, the strongest RR bands are in the region between 1000 and 1700 cm^{-1}, which includes the internal ring modes of the phenolate ligands as well as the C−O stretching vibrations. An interesting observation in the RR spectrum of the iron-oxo complex compared to the iron(III)–salen complex is that a dramatic decrease is observed in the intensities of all modes in the range of 1300, 1400 and 1600 cm^{-1}. In the case of Fe^{III}–porphyrin complexes, the reduced intensity has been attributed to the formation of porphyrin π-cation radical [18]. In addition to the above bands, a weak low frequency band at 839 cm^{-1} is observed for the iron-oxo complex. It is interesting to note that the low frequency spectrum of $[O{=}Fe^{IV}(TMP)]^{\bullet+}$ (TMP = tetramethylporphyrin) exhibits a polarized ν(Fe=O) mode at 835 cm^{-1}. The decrease in intensity of all peaks in the range 1300–1700 cm^{-1} has been taken as evidence for the formation of ligand cation radical. Thus, on the basis of the RR and UV–vis spectral study, the oxo(salen)iron complex is represented as $[O{=}Fe^{IV}(salen)^{\bullet+}]^+$. The ESIMS study also supports the formation of oxo(salen)iron ion but the chloride ion is detached from coordination site when oxo complex is generated from $[Fe^{III}(salen)]^+$ and PhIO [48,49]. Similar characteristics have been observed for oxo(salen)ruthenium ion [42].

2.2. Manganese

The discovery of Kochi–Jacobsen–Katsuki (KJK) catalyst for the epoxidation of olefins with a variety of oxidants provided a remarkably versatile and highly enantioselective method in organic synthesis [5–11,19–22,29,34–39,50–56]. The KJK system is superior to its porphyrin analogues and has attracted considerable pursuit in mimicking cytochrome P-450. Numerous experimental studies have demonstrated that [(salen)]Mn(III)$]^+$-derived species can easily oxidize alkenes and sulfides, while the nature and identity of the reactive species still need to be elucidated [50–58]. On the basis of the similarity to their porphyrin analogues, where the active species in oxidation reaction is believed to be the metal-oxo compound, the cationic oxo species $[(salen)Mn(V)(O)]^+$ has been postulated to be the active oxidant [40–42,59–62]. This has been supported by the characterization of the $[(salen)Cr(V)(O)]^+$ ion [19] and of the isoelectronic [(salen)Mn(V)(N)] [61]. Although claims of detecting $[(salen)Mn(V)(O)]^+$ species have been made recently by ^{1}H NMR [63] and ESIMS [64–67] spectral methods, both have deficiencies. Furthermore, several research teams recently paid attention to the transformation of the cationic $[(salen)Mn(V)(O)]^+$ to the neutral species [(salen)Mn(IV)(O)] in the absence of substrate [68,69]. The species [(salen)Mn(IV)(O)] exhibits characteristic ESR spectrum and oxidizes olefins via a stepwise radical mechanism. Although the build up of [(salen)Mn(IV)(O)] in the presence of substrate is unlikely, such species could certainly play a principal role at high conversion and with rigid substrates. In addition to monomeric species, several dimers such as Mn(III)Mn(IV) and Mn(IV)Mn(IV) have been reported to be involved in the reaction as well [63,65–67,70]. Thus, a number of species besides $[(salen)Mn(V)(O)]^+$ ion could form in the reaction conditions and should be taken into account in the interpretation of experimental data. Till now, no structural information is experimentally available for $[(salen)Mn(V)(O)]^+$ ion, while an estimate of its geometry has been obtained from the X-ray data of $[(salen)Cr(V)(O)]^+$ [19] and [(salen)Mn(V)(N)] [61]. In elucidating the geometric and electronic structures of the transient intermediates, one of the best approaches is the quantum mechanical calculation. Recently, several density functional studies on the geometric and electronic structures of the complex $[(salen)Mn(V)(O)]^+$ have been published [33,50–52,71–75].

In our studies, the formation of oxo(salen)manganese(V) species from $[(salen)Mn^{III}]^+$ and PhIO is associated with the following two changes: (i) the light brown colour gets darkened; and (ii) the characteristic peak of Mn(III)–salen ion at λ_{max} = 350 nm disappears and a new absorption band with λ_{max} = 530 nm appears. The new absorption band with λ_{max} = 530 nm has been assigned to μ-oxomanganese(IV) dimer, which is in equilibrium with Mn(III) and Mn(V) ions (Eq. (1)):

$$[O{=}Mn^{V}(salen)]^+ + [Mn^{III}(salen)]^+ \rightleftharpoons [(salen)Mn^{IV}OMn^{IV}(salen)]^{2+} \quad (1)$$

However, Mn^V and Mn^{IV} species are spectroscopically indistinguishable. The disproportionation of the μ-oxo(salen)manganese(IV) dimer back to the active oxo(salen)manganese(V) in Eq. (1) clearly indicates that the μ-oxodimer merely serves as an alternative source of oxo(salen)manganese(V) ion. Thus, oxo(salen)manganese(V) ion behaves solely as the oxidant for the oxidation of organic substrates in our study when PhIO is the oxygen source.

Apart from PhIO, H_2O_2 and ^-OCl have also been used as oxygen sources [41,44,57]. Reaction of oxygen atom transfer from H_2O_2 and alkyl hydroperoxides is generally slow and often complicated by radical chain reactions [76]. In previous reports of metal complexes catalysed oxidation studies with peroxides, metal-oxo, and metal-peroxo and in some cases, metal-independent peroxo or peroxy radicals have been proposed as reactive intermediates [52]. Manganese complexes, among a set of metal complexes containing the same ligand, behave peculiarly by not preferring the metal-independent reactive species in oxidation reactions catalysed by them [77]. The fact that the metal derived oxidizing species is established by the changes in the reaction rate with respect to changes in electronic and steric environment of the Mn(III)–salen complexes (vide infra). The development of a new absorption band with $\lambda_{max} \sim 420$ nm on mixing H_2O_2 with Mn(III)–salen complex and the subsequent decay of this band on adding organic sulfide indicates that this new species having λ_{max} value at 420 nm might be the species responsible for the oxidation. The absence of a band at $\lambda_{max} \sim 530$ nm, which is observed in the Mn(III)–salen/PhIO system, clearly shows that the oxidizing species here is not oxo(salen)manganese(V) ion. By comparing the spectral observations with earlier reports, it is concluded that the active species responsible for the oxidation is probably a manganese(III) hydroperoxide species, [(salen)Mn^{III}OOH] and its formation is expressed in Eq. (2):

$$[(\text{salen})Mn^{III}]^+ + H_2O_2 + H_2O \rightarrow [(\text{salen})Mn^{III}OOH] + H_3O^+ \quad (2)$$

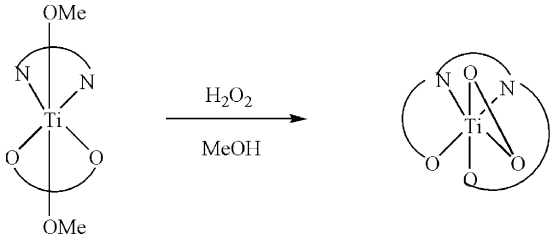
A similar [Mn^{III}OOH] complex as an active species has been postulated in the [(TPP)Mn^{III}Cl] catalysed epoxidation of olefins with H_2O_2 [78]. When ^-OCl is used as he oxidant the formation of a peak with absorption maximum at 530 nm is taken as the spectral evidence for $[(\text{salen})Mn(V)(O)]^+$ as the active oxidizing species [44].

2.3. Chromium

As far as chromium–salen complexes are concerned, the Cr(III)–salen ion is readily converted to the corresponding oxochromium(V) species by iodosylbenzene under the reaction conditions of the catalytic process [11,19,29,31,32,35–37,43]. The oxochromium(V) ion has been isolated as a single crystal suitable for X-ray crystallography from the treatment of chromium(III)–salen complex and PhIO, followed by precipitation with diethyl ether and recrystallization from a mixture of acetonitrile and chlorobenzene [19]. The ORTEP diagram clearly shows the presence of the oxo functionality on the chromium centre displaced ~0.5 Å above the mean salen plane to describe a roughly square-pyramidal coordination [19]. The oxo-chromium functionality is characterized by an infrared absorption (stretch) at 1003 cm^{-1}, which is displaced to 963 cm^{-1} upon isotopic substitution with ^{18}O. Furthermore, the presence of d^1 electron characteristic of a chromium(V) complex is indicated both by the magnetic susceptibility of 1.85μ_B and an isotropic ESR spectrum showing well-resolved nitrogen (a_N = 2.15 G) and chromium (a_N = 19.35 G, I = 3/2 for ^{53}Cr in 9.55% natural abundance) splitting centred at $\langle g \rangle$ = 1.978 at 25 °C [19,31,32].

2.4. Titanium

Oxo(salen)titanium ion has been generated using hydrogen peroxide as a terminal oxidant [79,80]. The X-ray diffraction analysis made on the complex formed from titanium–salen and hydrogen peroxide shows a *cis*-β structure corresponding to a di-μ-oxoTi(salen). However, in methanolic solution, a monomeric Ti(salen) is formed by a rapid alkoxide switch over and this reacts with hydrogen peroxide or urea–hydrogen peroxide (UHP) to give the corresponding peroxo species (Eq. (3)):



(3)

2.5. Vanadium

The use of vanadium complexes as oxidants is of unique interest and early work in this regard opened up new vistas to use the other transition metal complexes for the said purposes. The oxo functionality of oxo vanadium complexes take part in a number of interesting oxo-transfer reactions. Nakajima and co-workers [81] have reported the preparation and characterization of optically active Schiff base oxo-vanadium(IV) and oxo-vanadium(V) complexes (Figs. 1 and 2) and studied their catalytic properties.

3. Redox potentials of metal–salen complexes

One of the attractive features of salen-based ligand is that the ligands may be tuned both sterically and electronically by the variation of corresponding diamines and salicylaldehyde ligand precursors. Recent studies carried out by others [22] and us [30–32,42] revealed that alterations in the electronic properties of the substituents at the 5,5′-position of the catalyst can have profound effect. To quantify the influence of 5,5′-substituent on the oxidation reaction, reduction potentials of metal–salen complexes with electron-donating and electron-withdrawing groups have been evaluated and the data are given in Table 1.

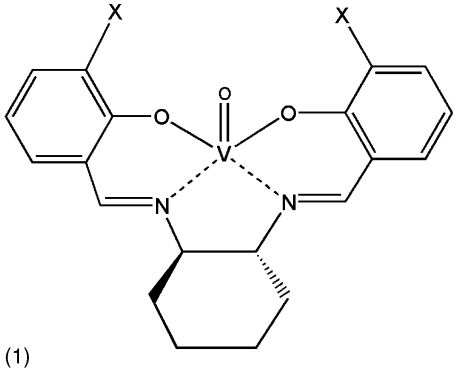
Table 1
Reduction potential of metal(III)–salen complexes and oxo(salen)chromium(V) complexes in the presence of electron releasing and withdrawing substituents in the salen ligand[a]

Iron		Ruthenium		Manganese		Chromium	
Complex	E_{red} vs. SCE (V)	Complex	E_{red} vs. SCE (V)	Complex	E_{red} vs. SCE (V)	Complex	E_{red} vs. SCE (V)
Ia	−0.28	**IIIa**	−0.72	**Va**	−0.45	**VIIIa**	+0.44
Ib	−0.15	**IIIb**	−0.66	**Vb**	−0.59	**VIIIb**	+0.40
Ic	−0.24	**IIIc**	−0.76	**Vc**	−0.35	**VIIIc**	+0.60
Ie	−0.30	**IIId**	−0.84	**Vd**	−0.08	**VIIId**	+0.60
If	−0.68					**VIIIe**	+0.24
						VIIIh	+0.45
						VIIIi	+0.61
						VIIIj	+0.22

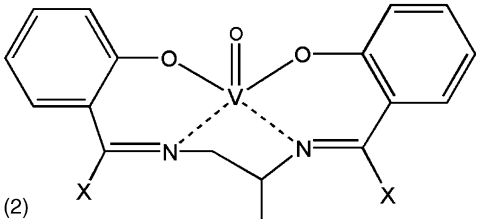
[a] For iron, ruthenium and manganese complexes, the reduction potentials of the couple M(III)/M(II) and for chromium complexes the reduction potentials of the couple M(V)/M(IV) are given.

Only in the case of Cr, the oxo(salen)chromium(V) ion is stable and characterized without any ambiguity. On the other hand, oxo-metal ions of Mn, Fe and Ru have transient existence. Interestingly, the reduction potentials of metal(III)–salen complexes and oxo(salen)chromium(V) complexes correlate well with the Hammett's σ constants [22,31,32,42]. Thus, the systematic variation in the reactivity of oxo(salen)metal ions with the change of substituent in the salen ligand can be rationalized in terms of redox potentials.

From the mechanistic point of view, this significant electronic effect on the reactivity of oxometal ion may be ascribed to any of the several factors. One of the possibilities is that substituents may effect changes in the metal-oxo bond length in the active species in turn altering the non-bonding ligand interactions in the relevant states. However, such effects on metal-oxo bond length are typically less pronounced [82]. An alternate explanation is that the electronic effect on the oxidation derives from alterations in the reactivity of the metal-oxo intermediate exerted by the substituents on the catalyst. Electron-donating substituents on the catalyst would be expected to stabilize the high valent metal-oxo intermediate attenuating its reactivity and then generating a relatively milder oxidant. Similarly, electron-withdrawing substituents on the catalyst are expected to destabilize the metal-oxo intermediate making it a more reactive oxidant. These results of electrochemical studies on catalyst [22,30–32,84] provide credence to this supposition. There is a clear correlation between σ_p of the 5,5′-substituent and the value of $E_{1/2}$ for the Mn(II)/Mn(III), Fe(II)/Fe(III), Ru(II)/Ru(III) and Cr(IV)/Cr(V) redox couples. Accurate measurement of the redox potentials for higher metal oxidation states in the case of Mn, Fe and Ru was precluded by the instability of M(IV) and M(V) species under the electrochemical reaction conditions.



(1)



(2)

Figs. 1 and 2. Oxo(salen)vanadium(IV) and oxo(salen)vanadium(V) complexes.

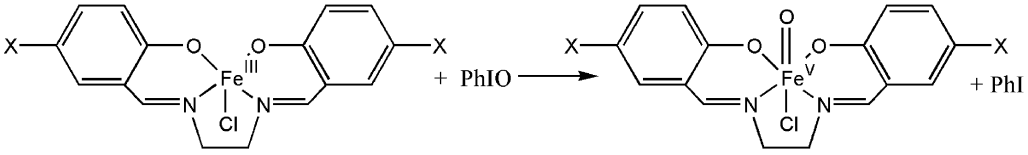
In accordance with the Hammond postulate, a milder oxidant should lead to an oxygen transfer to substrate via a more product-like transition state since this conversion involves the encounter of two reactants, which at the origin of the reaction coordinate do not interact at all. Oxo transfer from a more reactive oxidant, on the other hand, should proceed via a more reactant-like transition state with greater spatial separation between substrate and catalyst and consequently poorer differentiation of diastereomeric transition structures. These postulations have been verified extensively in the epoxidation reaction but little attempt has been made on sulfoxidation [22].

4. Oxidation of organic sulfur compounds—synthesis and mechanism

4.1. Iron and ruthenium

In recent reports [30,49], we have described the synthesis and characterization of several oxo(salen)iron complexes as

represented in Eq. (4):



Ia-f **IIa-f**

a: unsubstituted, **b**: 5,5'-$(NO_2)_2$, **c**: 5,5'-Cl_2
d: 5,5'-$(OCH_3)_2$, **e**: 7,7'-$(CH_3)_2$, **f**: 3,3',5,5'-$(t\text{-Bu})_4$ (4)

The oxygenation of organic sulfides to sulfoxides with oxo(salen)iron complexes **IIa–f** in CH_3CN proceeds through saturation kinetics implying that the reaction proceeds through Michaelis–Menten type mechanism (Eqs. (5) and (6)):

$$\text{oxidant} + \text{substrate} \rightleftharpoons \text{complex} \quad (5)$$

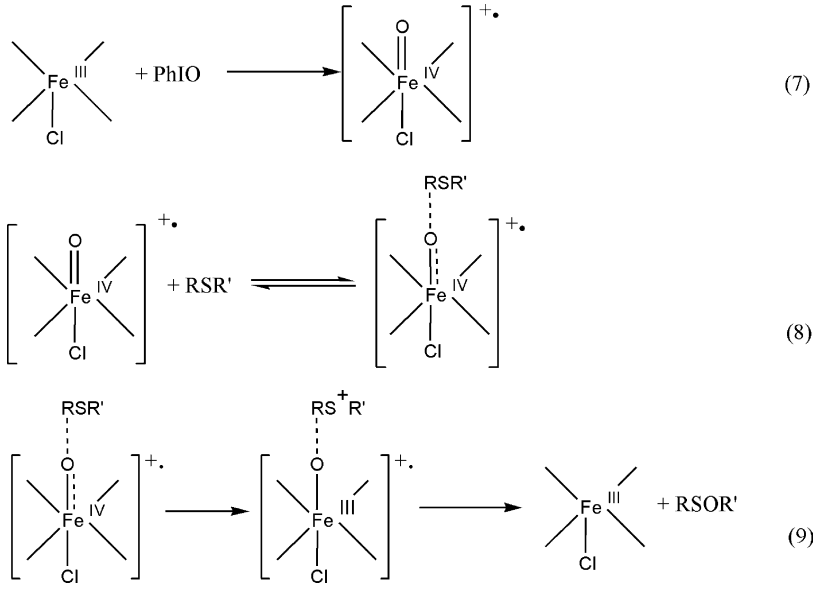
$$\text{complex} \xrightarrow{k} \text{product} \quad (6)$$

The electron-donating substituents present in the *para*-position of the phenyl ring of PhSMe accelerate the rate and the electron-withdrawing groups decelerate it. The k values are analysed in terms of the Hammett equation and the reaction constant (ρ) value is in the range of −0.65 to −1.54 for different oxo(salen)iron complexes. The effect of introducing substituent in the salen ligand had the opposite effect on the rate of oxidation and the ρ value is positive ($\rho = 0.8$).

The saturation kinetics observed here and low Michaelis–Menten constant, K_M values indicate strong binding of substrate with the oxidant. The k/K_M values are in the range 0.2–1.6 with **IIb** and these values are better than the values observed with HRP and human cytochrome P-450 A_{12} [83,84]. The slope values in the range of −1.70 to −2.92 from the plots of log k versus E_{ox} was observed by Goto et al. [85] and a mechanism for the reaction proceeding via direct oxygen transfer was postulated (Scheme 1).

To check the utility of these oxo(salen)iron complexes as useful reagents, the percentage yield of sulfoxide formed from the oxidation of sulfide has been measured. The conversion of sulfide to sulfoxide is efficient and selective and depends on the nature of the substituent in the oxidant and substrate that support the proposed mechanism (Scheme 1). The yields of sulfoxides formed from the selective oxygenation of *p*-XC_6H_4-S-CH_3 with iron–salen complexes are collected in Table 2.

Six oxo(salen)iron complexes (**IIa–f**) have also been used for the oxidation of organic sulfoxides which may undergo either electrophilic or nucleophilic oxidation depending on the nature of the oxidant [86–88]. Further, sulfoxides are less powerful nucleophiles compared to organic sulfides [89]. Towards oxo(salen)iron complexes, the organic sulfoxides behave as nucleophiles and are oxidized to the corresponding sulfones. The kinetic results obtained for the oxidation of organic sulfoxides with **IIa–f** are very similar to those ob-



Scheme 1. Proposed mechanism for sulfide oxidation by iron–salen complexes.

Table 2
Yields of sulfoxides formed from the oxygenation of *p*-XC_6H_4-S-CH_3 in CH_3CN at 298 K by oxo(salen)iron complexes, **IIa** and **IIb**[a]

X	IIa		IIb	
	Reaction time (min)	Sulfoxide (%)	Reaction time (min)	Sulfoxide (%)
H	120	88	60	100
OMe	90	85	50	100
Me	120	100	60	100
F	120	95	60	85
Cl	120	78	60	75
Br	120	77	60	68
$COCH_3$	120	39	60	70
CN	140	41	80	47
NO_2	140	49	80	43

[a] For the details of the structure of oxo(salen)iron complexes, refer Eq. (4).

served for the oxidation of organic sulfides, i.e., the reaction proceeds through Michaelis–Menten kinetics. The reaction constant (ρ) values are less for organic sulfoxides and are in the range of −0.43 to −0.85. Thus, organic sulfoxides are less reactive and less sensitive to the change of substituents in the *para*-position of phenyl ring of PhS(O)Me. Based on these observations, a mechanism similar to the one shown in Scheme 1 has been postulated for the oxo(salen)iron complexes oxygenation of organic sulfoxides.

Recently, there has been an upsurge of interest on the redox reactions of ruthenium-oxo complexes with organic substrates [90]. Owing to the periodic relationship between ruthenium and iron, the chemistry of ruthenium porphyrins has been subjected to extensive study as models for reactive cytochromes. We have used four oxo(salen)ruthenium(V) complexes (**IVa–d**) generated in situ from a series of Ru^{III}(salen)(PPh_3) complexes, **IIIa–d** and PhIO (Eq. (10)) for the oxidation of organic substrates:

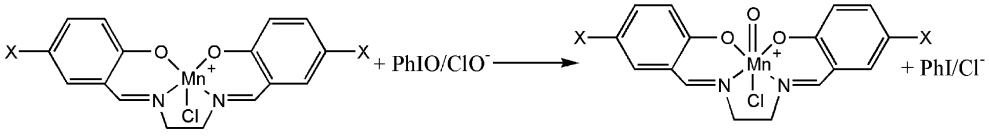
$$\underset{\textbf{IIIa–d}}{[Ru^{III}(5,5'\text{-}X_2\text{salen})(PPh_3)(CH_3CN)]} + PhIO \rightarrow \underset{\textbf{IVa–d}}{[O{=}Ru^{V}(5,5'\text{-}X_2\text{salen})(PPh_3)]^{+}} + PhI + CH_3CN \quad (10)$$

where **a**: unsubstituted; **b**: 5,5′-$(OCH_3)_2$; **c**: 5,5′-Cl_2; **d**: 5,5′-$(NO_2)_2$.The Ru(III)–salen and oxo(salen)ruthenium(V) complexes have been characterized by UV–vis and IR spectral techniques. Organic sulfides are oxidized efficiently by oxo(salen)ruthenium(V) complexes to the corresponding sulfoxides. The fractional order dependence and the saturation kinetics observed with respect to the substrate indicate reversible complex formation between the oxidant and the substrate. The rate constants for the decomposition of the oxidant–substrate complex evaluated from the Lineweaver–Burk plots correlate better with σ^+/σ^- values ($r = 0.996$, $\rho = -0.60$) rather than Hammett's σ values ($r = 0.965$, $\rho = -0.99$). To account for the spectral and kinetic data, a mechanism similar to Scheme 1 has been proposed for the oxo(salen)ruthenium ion oxygenation of organic sulfides.

4.2. Manganese

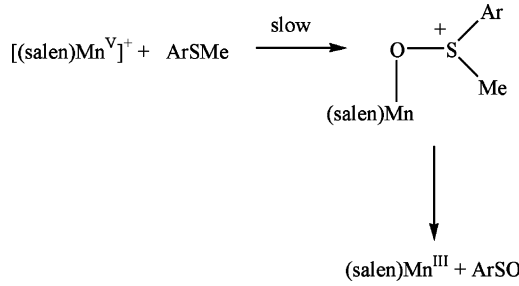
The first report on the sulfoxidation reaction using Mn(III)–salen complexes as catalysts and H_2O_2 as the oxidant is from the laboratory of Jacobsen and co-workers [57]. This group recommended the use of H_2O_2 as a terminal oxidant to prevent over oxidation to sulfones in the oxidation of sulfides. However, Katsuki and co-workers [6,21,58] proved that H_2O_2 is not a good terminal oxidant. In all cases, the use of H_2O_2 led to considerably lower chemical yields as compared with PhIO. After many trials for years, Katsuki's group synthesized a complex bearing methoxy group in the salicylaldehyde part and found that complex showed the remarkably enhanced asymmetric induction (62% ee) and that the ratio of sulfoxide to sulfone was improved to 6.9:1. In order to improve the enantioselectivity of sulfoxide, Katsuki and co-workers added donor ligands such as pyridine *N*-oxide (PyO). Surprisingly, all the ligands examined showed the negative effect on enantioselectivity, though the ratio of sulfoxide to sulfone was further improved to 4:1 when PyO was used [39].

In the past decade, we have carried out the work on the oxidation of organic sulfides and sulfoxides using PhIO, H_2O_2 and ClO^- as oxidants and several Mn(III)–salen complexes as catalyst [40–42,44]. It is interesting to point out the different kinetic features shown by H_2O_2 and PhIO/ClO^- towards the oxidation of organic sulfides. The Mn(III)–salen ion catalysed PhIO/ClO^- oxidation of organic sulfides proceeds by clean second-order kinetics, first order each in the oxidant and substrate. In this reaction, oxo(salen)manganese(V) ion (**VI**) is generated by stirring a clear brown solution of Mn(III)–salen complexes (**V**) in CH_3CN with PhIO/ClO^- (Eq. (11)):



Va-f **VIa-f**

a. X = H, **b**. X = OCH_3, **c**. X = Cl_2
d. X = NO_2, **e**. X = CH_3, **f**. X = C_6H_5 (11)



Scheme 2. Proposed mechanism for manganese–salen catalysed sulfoxide oxidation.

The $\log k_2$ values of *meta*- and *para*-substituted phenyl methyl sulfides vary linearly with σ_p giving ρ values in the range of −1.4 to −2.1. The negative value of ρ indicates an accumulation of positive charge at the sulfur centre, while the magnitude of ρ value indicates the extent of charge development on the sulfur atom in the transition state. Hammett correlation of $\log k_2$ versus $\sum \sigma_p$ (where σ_p is the Hammett substituent constant for each of the *para*-substituents in the salen ligand) shows a linear relationship giving positive ρ value ($\rho = 0.48$) indicating the build-up of negative charge on the metal centre in the transition state. To account for the spectral and kinetic data, a mechanism involving electron transfer from the substrate to the oxidant instead of shown in Scheme 2 has been postulated.

A clear picture on the mechanism (Scheme 3) of the oxygenation of organic sulfides and sulfoxides emerges from a comparison of results on organic sulfoxides with those observed for the oxo(salen)manganese(V) complexes oxidation of organic sulfides. The oxo(salen)manganese(V) ion oxygenation of organic sulfoxides follows second-order kinetics, first order in each reactant similar to the oxidation of organic sulfides. The $\log k_2$ values show better correlation with σ_p ($r = 0.997$, $\rho = -2.44$) than σ_p^+/σ_p^- ($r = 0.984$, $\rho^+ = -1.54$). The electronic effects on the reactivity of oxo(salen)manganese(V) complexes give a ρ value of 0.52. There is an excellent correlation between E° values of the Mn^{II}/Mn^{III} couple and $\sum \sigma_p$ of the 5,5′-substituents (slope = 0.24). Thus, the effect of introducing a 5,5′-substituent in the salen ligand on the redox potential of the metal-oxo complex is mainly responsible for the substituent effect on the rate of the oxygenation reaction.

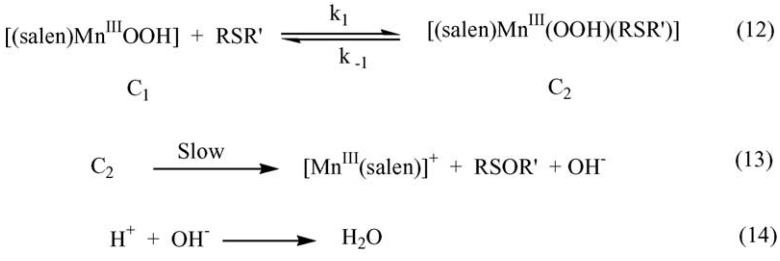
It is surprising that the reactivity of organic sulfides and sulfoxides towards these Mn(V) complexes is comparable and the ρ values are always higher with sulfoxides. These data are in accordance with the Hammond postulate i.e., consistent with a common S_N2 mechanism wherein only the position of the transition state changes from one substrate class to the next. The more electron-rich sulfides should have an earlier transition state for interaction with an electrophilic metal-oxo complex and will thus exhibit less charge on S and a weaker influence of the substituent, leading to a low ρ value. The reverse is the case with less nucleophilic substrates, sulfoxides giving a fairly higher ρ value. Based on these arguments, a common mechanism shown in Scheme 2 has been proposed for oxo(salen)manganese(V) ion oxygenation of organic sulfides and sulfoxides.

A different mechanism (Scheme 3) is proposed for the oxidation of sulfides by H_2O_2 in the presence of Mn(III)–salen complexes. The proposed mechanism involves the reversible formation of an intermediate complex (C_2) between C_1 and sulfide. Then the intermediate complex C_2 decomposes to give $(salen)Mn^{III}$ ion and sulfoxide in the rate determining step. The correlation of $\log k_2$ of *p*-XC_6H_4-S-Me with Hammett's σ_p values shows excellent linearity ($r = 0.994$) yielding a ρ value of −0.85. The low ρ value −0.85 observed in this reaction may be due to the weak electrophilic character of the oxidant (C_1) than the oxo(salen)manganese(V) ion which gives a ρ value of −1.85 in the oxidation of aryl methyl sulfides.

4.3. Chromium

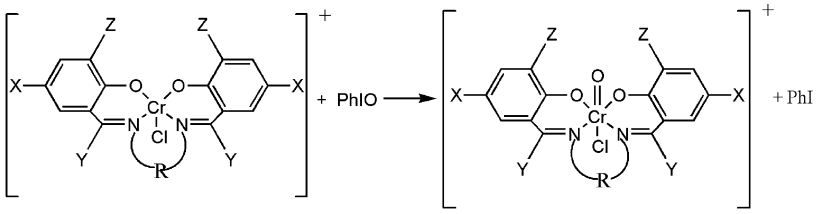
As far as the biological importance of metal ions are concerned, iron and manganese have well developed bioinorganic chemistry [46]. On the other hand, still there is debate on the role of chromium whether it is an essential trace element for mammals or not. Nonetheless, it has been shown that trivalent chromium (Cr^{3+}) is actually an essential nutrient, needed for the expression of glucose tolerance [91,92]. Apart from this biological relevance of these Cr^{3+} complexes, Cr(III)–salen complexes have been extensively used as catalysts for the oxidative transformations of a variety of organic substrates [11,23,24,31–37]. The role of $[Cr^{III}(salen)]^+$ as a bridge between asymmetric catalysis, Lewis acids and redox processes is projected recently in a feature article by Bandini et al. [11].

In recent years, we have generated oxo(salen) chromium(V) ions (**VIIIa–j**) from Cr(III)–salen com-

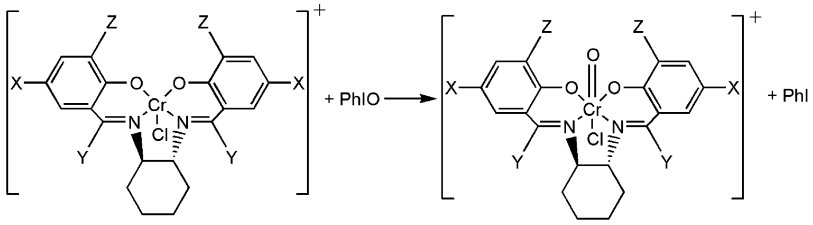


Scheme 3. Proposed mechanism for manganese–salen catalysed sulfide oxidation in the presence of hydrogen peroxide.

plexes (**VIIa–j**) and PhIO (Eqs. (15) and (16)) and used them for the oxygenation of organic sulfides and sulfoxides in the presence and absence of donor ligands like pyridine *N*-oxides, imidazole, etc. [31,32,43]:



VIIa, VIIIa: X = H, Y = H, Z = H, R = -CH_2-CH_2 **VIIb, VIIIb**: X = CH_3, Y = H, Z = H, R = -CH_2-CH_2
VIIc, VIIIc: X = Cl, Y = H, Z = H, R = -CH_2-CH_2 **VIId, VIIId**: X = Br, Y = H, Z = H, R = -CH_2-CH_2
VIIe, VIIIe: X = *t*-Bu, Y = H, Z = *t*-Bu, R = -CH_2-CH_2 **VIIf, VIIIf**: X = H, Y = CH_3, Z = H, R = -CH_2-CH_2
VIIg, VIIIg: X = H, Y = H, Z = H, R = -CH_2-CH_2-CH_2 **VIIh, VIIIh**: X = H, Y = H, Z = H, R = -C_6H_4 (15)



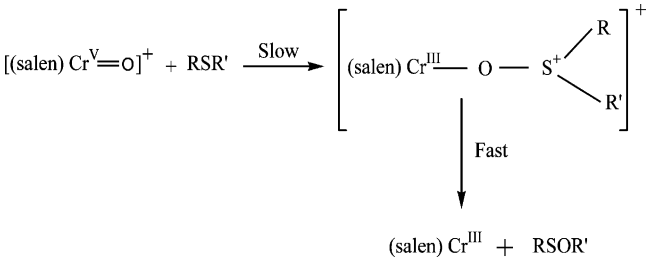
VIIi, VIIIi: X = Z = H **VIIj, VIIIj**: X = Z = *t* - Bu (16)

The oxygenation of organic sulfides with **VIIIa–j** is overall second order, first order with respect to the oxidant and the substrate. Kinetic studies in different ratios of solvent systems (CH_3CN–H_2O) revealed that the influence of solvent on the rate is substantial; this increase may not only to a change in polarity but also due to other effects. The addition of H_2O shifts λ_{max} of $[O{=}Cr^{V}(salen)]^{+}$ from 560 to 600 nm. Thus, H_2O is coordinated to the metal and it is likely to act as the axial ligand enhancing the rate substantially.

The analysis of kinetic data observed for *p*-XC_6H_4-S-Me with the Hammett equation gives negative ρ values in the range −1.14 to −2.72. From the recent literature, it is known that oxygen atom transfer to organic sulfides from oxo-metal complexes proceeds generally by two different mechanisms, single-electron transfer from the substrate to the oxidant and S_N2 mechanism [93]. However, a twofold mechanism has been proposed in some oxidation reactions [94]. In the present study, the nucleophilic attack of sulfide on the Cr centre may be excluded, as it is difficult to explain the formation of sulfoxide from such a formulation. The coordination of the substrate to the metal is not significant, which is evident from the following observations: (i) When the substrate is added to $[O{=}Cr^{V}(salen)]^{+}$, there is little change in the absorption spectrum of the latter. Addition of trichloroacetic acid, H_2O and donor ligands such as imidazole and pyridine *N*-oxide to $[O{=}Cr^{V}(salen)]^{+}$ produces a substantial shift in the λ_{max}. (ii) The reaction is clearly first order in the substrate and no saturation kinetics with respect to substrate is observed. When the reaction between $[O{=}Cr^{V}(salen)]^{+}$ and PhSMe was carried out at different concentration of Mn^{II}, no substantial change in the *k* value was observed. This observation rules out the formation of Cr^{IV} in the rate-controlling step. The higher reactivity of diethyl sulfide ($E_{1/2}$ = 1.65 V) compared to PhSMe (E° = 1.53 V) also rules out the operation of electron-transfer mechanism. Thus, a mechanism involving the electrophilic attack of oxygen at the sulfur centre of the organic sulfide (Scheme 4) has been proposed. However, an electron-transfer mechanism has been proposed by Lee and co-workers [95]. The yields of sulfoxides formed from the selective oxygenation of organic sulfides by oxo(salen)chromium complexes are given in Table 3. The transition state of the reaction may be represented as shown in Fig. 3.

The study has been extended to the oxo(salen) chromium(V) ion oxidation of organic sulfoxides. Interestingly sulfoxides bind with Cr(V) ion and the absorption maximum, λ_{max}, of Cr(V) ion shifts from 560 to 606 nm and the peak sharpens (Fig. 4).

From these spectral studies, it is realized that DMSO and aryl methyl sulfoxides bind with all Cr(V)–salen complexes.



Scheme 4. Proposed mechanism for chromium–salen catalysed sulfide oxidation.

Table 3
Yields of sulfoxides formed from the selective oxygenation of p-XC_6H_4-S-CH_3 with chromium–salen complexes, **VIIIa** and **VIIIg–j** in CH_3CN at 298 K[a]

X	**VIIIa**		**VIIIg**		**VIIIh**		**VIIIi**		**VIIIj**	
	Reaction time (min)	Sulfoxide (%)	Reaction time (min)	Sulfoxide (%)	Reaction time (min)	Sulfoxide (%)	Reaction time (min)	Sulfoxide (%)	Reaction time (min)	Sulfoxide (%)
H	240	96	150	99	180	82	180	96	300	96
OMe	60	95	25	99	150	92	135	100	180	100
Me	75	93	25	90	160	88	135	98	240	98
F	200	78	120	70	180	65	150	72	300	72
Cl	240	60	150	55	240	68	180	49	320	49
Br	240	61	150	57	240	55	180	52	350	52
$COCH_3$	240	40	150	42	400	59	180	61	380	61
COOH	240	30	150	27	400	51	180	45	380	45

[a] For the details of the structure of oxo(salen)chromium(V) complexes, refer Eq. (15).

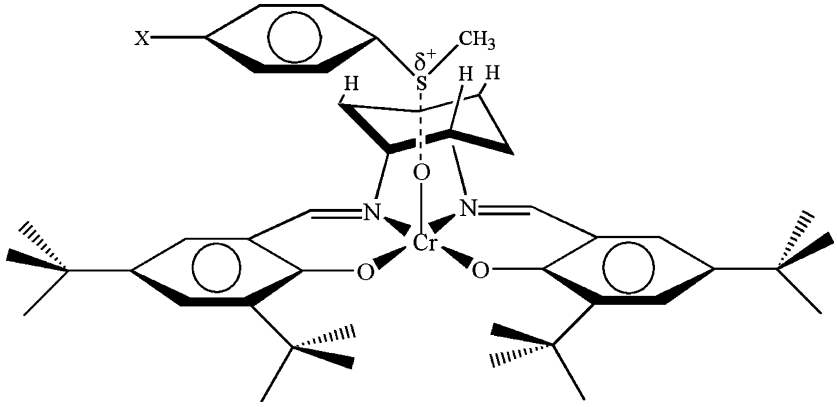


Fig. 3. Transition state for the electrophilic attack of oxygen on electron-rich sulfur represented in Scheme 5. The oxo(salen)chromium(V) complex is **VIIIj**.

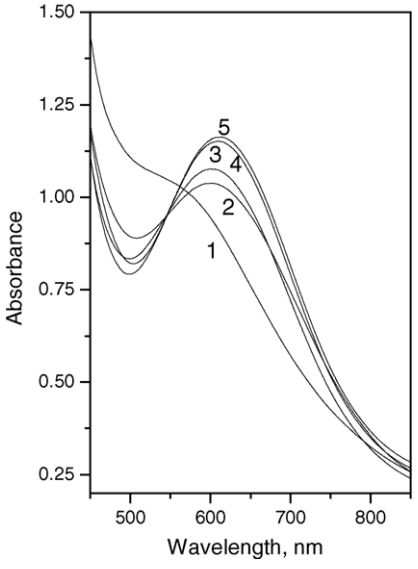
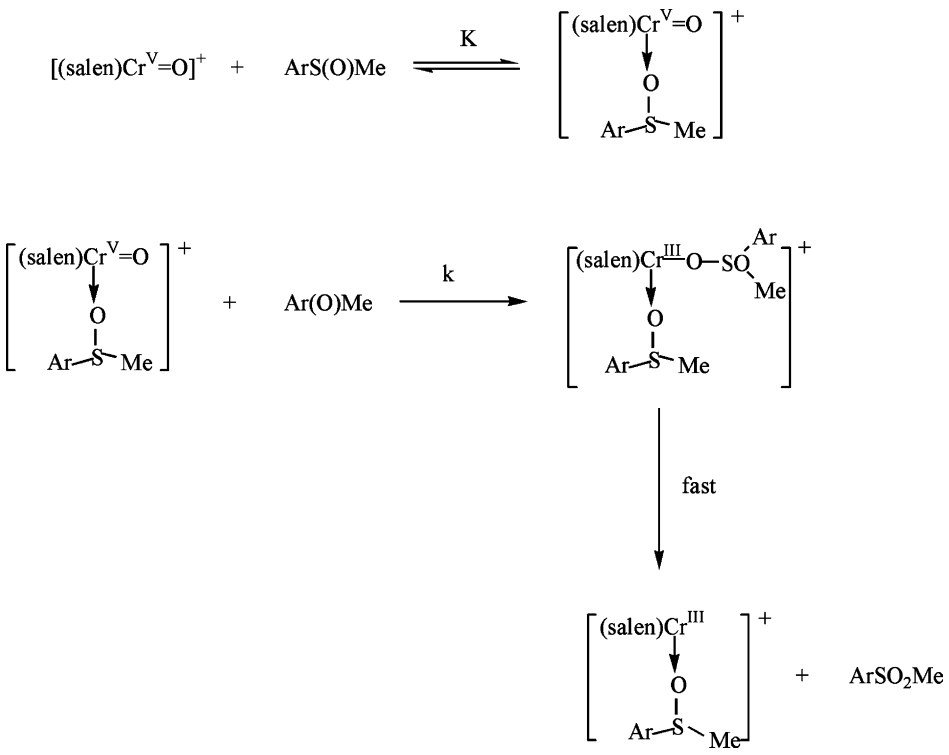


Fig. 4. Absorption spectra of **IIc** (4×10^{-4} M) in the presence and absence of LO. (1) In the absence of LO; (2) in the presence of 0.1 M DMSO; (3) in the presence of 0.001 M Pic NO; (4) in the presence of 0.1M PyO; (5) in the presence of 0.01 M TPPO.

Interestingly, the bound sulfoxides act as donor ligands to catalyse the oxidation of organic substrates [96]. When MPSO and DMSO are added to oxo(salen)chromium(V) ions, a shift in the λ_{max} value to the tune 10–60 nm is observed and the OD of Cr(V) ion increases with the increase in [sulfoxide] and it attains the maximum OD at [MPSO] = 0.1 M. This behaviour of oxo(salen)chromium(V) ion differs from that of oxo(salen)manganese ion toward sulfoxide. The increase in OD with [sulfoxide] has been utilized to estimate the binding constant of sulfoxides with oxo(salen)chromium(V) ion and the binding constant values are in the range 10–150 M^{-1}. From the absorption spectrum of Cr(V) ion in the presence of sulfoxide at different time intervals, it is realized that the oxygenation reaction takes place after the binding of the substrate to the oxidant. From these experimental observations, it is proposed that the first step of the mechanism involves binding of sulfoxides to the chromium centre of the oxidant. Here, sulfoxide has a dual role, it acts as a donor ligand as well as a substrate [97,98]. Thus, the real oxidant in the present condition is the chromium(V)–sulfoxide adduct, which oxygenates the excess sulfoxide present in the system. Under the present experimental conditions, although three different modes of oxidation may be envisaged, the most probable mechanism is a bimolecular (outer sphere) electrophilic oxidation carried



Scheme 5. Proposed mechanism for sulfoxide oxidation by chromium–salen complexes.

out by oxidant–sulfoxide adduct at a non-ligated sulfoxide (Scheme 5). The strong binding of sulfoxide to the Cr centre weakens the Cr=O bond in the oxo(salen)chromium(V) ion facilitating oxygen transfer from the oxidant to the substrate [31].

4.4. Titanium

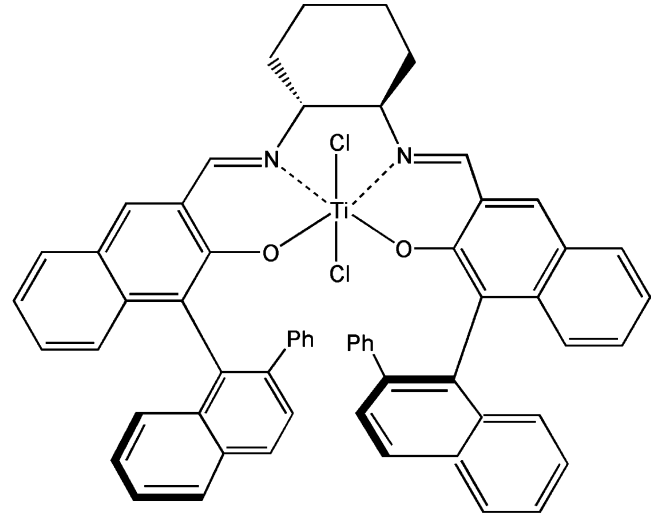
Saito and Katsuki [79,80] recently reported a highly enantioselective sulfoxidation using di-μ-oxoTi(salen) complex in methanol as the catalyst. FABMS and ^{1}H NMR spectral measurements showed that the square planar structure of the salen ligand is readily changeable to the *cis*-β structure when a bidentate ligand is coordinated to the titanium ion. The authors examined the sulfoxidation of MPS with di-μ-oxo complexes of different enantiomeric excesses, which were prepared by mixing (*R*,*R*)- and (*S*,*S*)-di-μ-oxo complex in methanol (Figs. 5 and 6). From this study, they have concluded that (*R*,*R*)-di-μ-oxo complex in methanol rapidly dissociates into a monomeric Ti(salen) complex and reacts with H_2O_2 to give the corresponding peroxo species which undergoes sulfoxidation (Scheme 6).

4.5. Vanadium

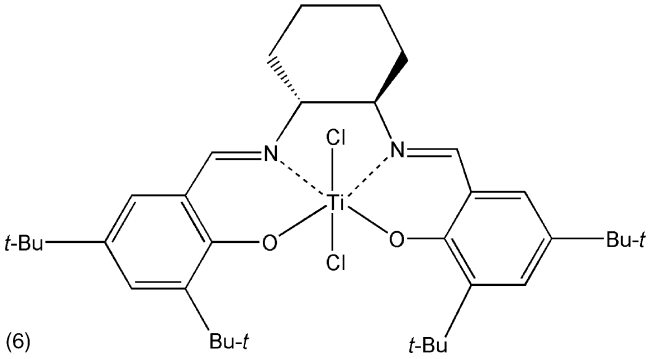
The oxidation of sulfides to sulfoxides by oxo-vanadium(IV) and oxo-vanadium(V) complex is almost complete and in many cases the optical yield (ee) ranges between 20 and 40% [81,99]. This reaction has been studied using a semi-synthetic vanadium peroxidase catalyst by Vande Velde et al. [100]. The ease of access of the active site of the peroxidase has been explored by comparing the results of oxidation of a series of *meta*- and *para*-substituted phenyl methyl sulfides as well as ethyl phenyl sulfides. Electron-withdrawing groups in the *para*-position of the phenyl ring of PhSMe lower the rate of oxidation and methyl or methoxy substituents result in a slight increase in the rate. The results are consistent with a rate limiting nucleophilic attack of the sulfur atom of the substrate on an electrophilic peroxo species (Scheme 7). Vanadium complexes can also activate molecular oxygen for oxygenation reactions and they have been described in a previous report [81,89,101]

4.6. Other metal ions

Miyazaki and Katsuki [102] studied the asymmetric sulfoxidation using chiral niobium complexes as catalysts. They prepared niobium–salen complexes in situ by mixing equimolar amounts of $NbCl_3$(dme) and salen ligands. The sense of asymmetric induction of these complexes is dictated by the chirality of their diamine unit and the chirality at the binaphthyl unit has a crucial influence on the magnitude of the asymmetric induction. They have also used niobium–chiral ligand complexes (Figs. 7 and 8) as catalysts. (a*S*,*R*)-**IXa** and (a*R*,*S*)-**Xa** are superior to (a*R*,*R*)-**IXb** and (a*R*,*R*)-**Xb** type of complexes.



(5)

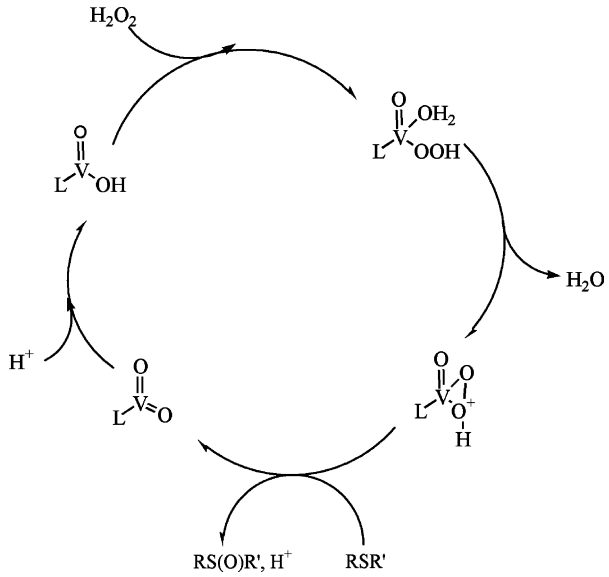


(6)

Figs. 5 and 6. (*R,R*)-Di-μ-titanium–salen and (*S,S*)-di-μ-titanium–salen complexes.

4.7. Comparison of metal complexes' oxidation of organic sulfur compounds

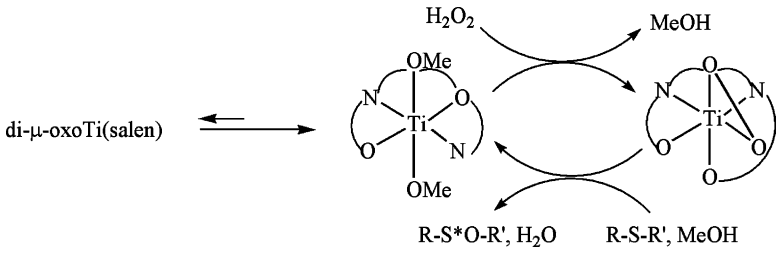
To get a clear picture on the electrophilicity of the oxo(salen)–metal complexes and the reactivity of these complexes toward biologically important substrates, organic sulfides and sulfoxides, we have used four metal ions, Fe, Ru, Mn and Cr. The metal ions Fe and Ru have similar behaviour. Chromium ion has a unique role because of its well-known utility in synthesis and its carcinogenicity [103,104]. If the reaction between Cr and organic substrates were to proceed through an electron-transfer mechanism, radicals would be



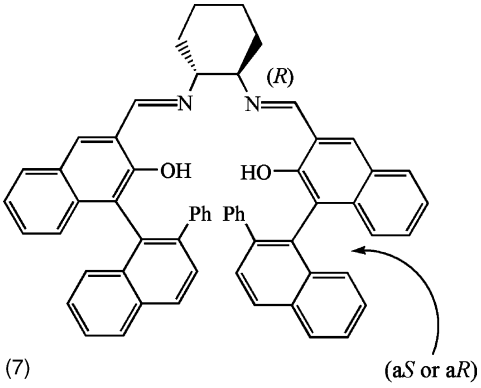
Scheme 7. Mechanism for vanadium–salen catalysed sulfide oxidation as proposed by Vande Velde et al. [100].

produced as intermediates, and the redox system is prone to greater toxicity. We have shown that oxo(salen)chromium(V) complexes oxidize organic sulfides selectively and the reaction proceeds through a clean bimolecular electrophilic oxidation reaction. Further, the results observed in our study show that organic sulfoxides have a dual role. When they are used as substrates toward oxo(salen)chromium(V) complexes, the sulfoxide binds with chromium(V) ion and thus operates as a donor ligand. Thus, chromium(V)–sulfoxide complex has the propensity to act as a catalyst for the oxidation of organic substrates. To check the catalytic role of organic sulfoxides, the kinetics of the reaction between oxo(salen)chromium(V) complexes and organic sulfides in the presence of MPSO have also been monitored. These data show that organic sulfoxide acts as a catalyst for the oxidation of organic sulfides. This catalytic activity of sulfoxides is similar to the role of PyO and Ph_3PO, and data obtained in the presence of PyO and Ph_3PO are included in Table 4.

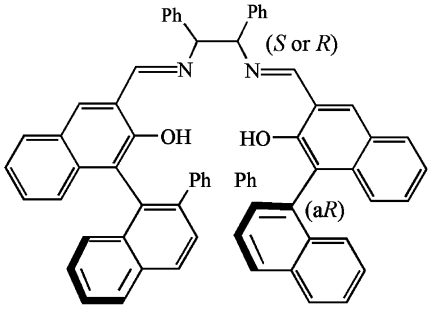
Further, donor ligands like PyO and Ph_3PO have diminutive effect on the oxygenation of organic sulfides with salen complexes of Mn and Fe [30,40–42]. However, in the case of Mn and Fe complexes, sulfoxides act only as substrates.



Scheme 6. Titanium–salen catalysed sulfoxidation as proposed Katsuki and co-workers [79,80].



IXa: (a*S, R)*
IXb: (a*R, R*)



Xa: (a*R, S)*
Xb: (a*R, R*)

Figs. 7 and 8. Chiral niobium–salen complexes.

It is worthwhile to recall that the electronic nature of the sulfoxide and its interaction with the metal atom play a key role in the global stereoselectivity of the sulfoxidation process. It is known that the over oxidation of sulfoxide to sulfone is pivotal in enhancing the enantiomeric excess of the sulfoxide by kinetic resolution [105]. The data given in Table 4 show that all donor ligands catalyse the Cr(V) oxidation of organic sulfides and the reaction constant (ρ) obtained with the catalysed reaction is always small compared to the uncatalysed oxidation.

5. Oxidation of organic nitrogen compounds

The oxidation of aromatic amines is complicated by the operation of several reaction paths. Not only substitution on nitrogen, but also hydrogen abstraction from nitrogen and addition of oxygen to carbon may occur. The predominant product seems to depend as much on the oxidant as on the structure of amine. Oxidative substitution of primary amines results in the formation of either hydroxylamines or amine oxides. Amines may also be oxidized by exclusion of an electron from the amine substrate by the oxidant thereby forming radical cations. These radical cations may undergo further reactions leading to dimer, oligomer and polymers according to the nature of the substrate. Enzymes such as peroxidases in the presence of H_2O_2 and laccases in the presence of oxygen catalyse the oxidation of anilines through free radical intermediates, which are known to participate in a variety of non-enzymatic reactions such as disproportionation, polymerization, and electron transfer [106]. Oxidative demethylation of *N*,*N*-dimethyl anilines catalysed by peroxidases also proceeds through ET from the amine to a high valent oxometal species.

5.1. Chromium

Oxo(salen)chromium(V) ions are particularly selective for the epoxidation and sulfoxidation reactions [11,19,29,31,43]. Realizing the importance of *N*-oxides, we have used oxo(salen)chromium(V) ions for the oxidation of primary, secondary and tertiary aromatic amines to get the corresponding *N*-oxides. Surprisingly, all the three types of aromatic amines lead to the formation of oligomers. The secondary and tertiary amines also undergo dealkylation reactions. The course of these reactions has been followed by UV–vis, ES-IMS and EPR spectral techniques.

Table 4
Rate constants obtained for the oxidation of X-C_6H_4-S-CH_3 by oxo(salen)chromium(V) ion **VIIIa** in the absence and presence of MPSO, PyO and Ph_3PO[a]

X	k_2 ($\times 10^3$ M^{-1} s^{-1})			
	Without donor ligand	With MPSO	With PyO	With Ph_3PO
H	1.31 ± 0.03	9.53 ± 0.07	37.3 ± 0.09	48.8 ± 0.08
p-OMe	25.9 ± 0.59	27.8 ± 0.82	90.9 ± 1.21	133 ± 1.3
p-Me	11.4 ± 0.23	19.8 ± 0.55	38.5 ± 0.89	105 ± 1.1
p-F	1.58 ± 0.08	7.51 ± 0.06	17.2 ± 0.24	27.4 ± 0.7
p-Cl	0.93 ± 0.01	5.33 ± 0.05	10.4 ± 0.12	18.5 ± 0.2
p-Br	0.93 ± 0.01	5.10 ± 0.02	9.77 ± 0.09	18.1 ± 0.1
p-CO_2H	0.24 ± 0.02	2.56 ± 0.01	4.68 ± 0.06	7.33 ± 0.07
p-$COCH_3$	0.16 ± 0.01	2.24 ± 0.01	4.69 ± 0.05	7.21 ± 0.05
ρ	−2.8	−1.5	−1.7	−1.8
r	0.965	0.991	0.989	0.994

[a] For the structure of oxo(salen)chromium(V) complex (**VIIIa**), refer Eq. (15).

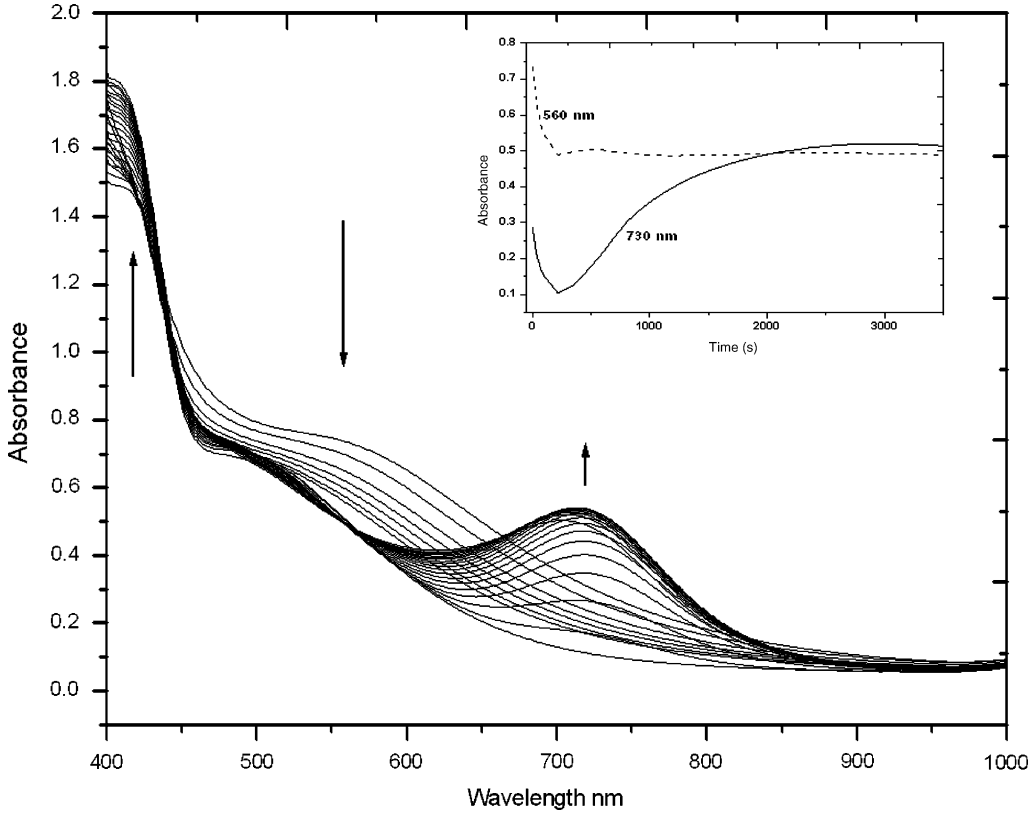
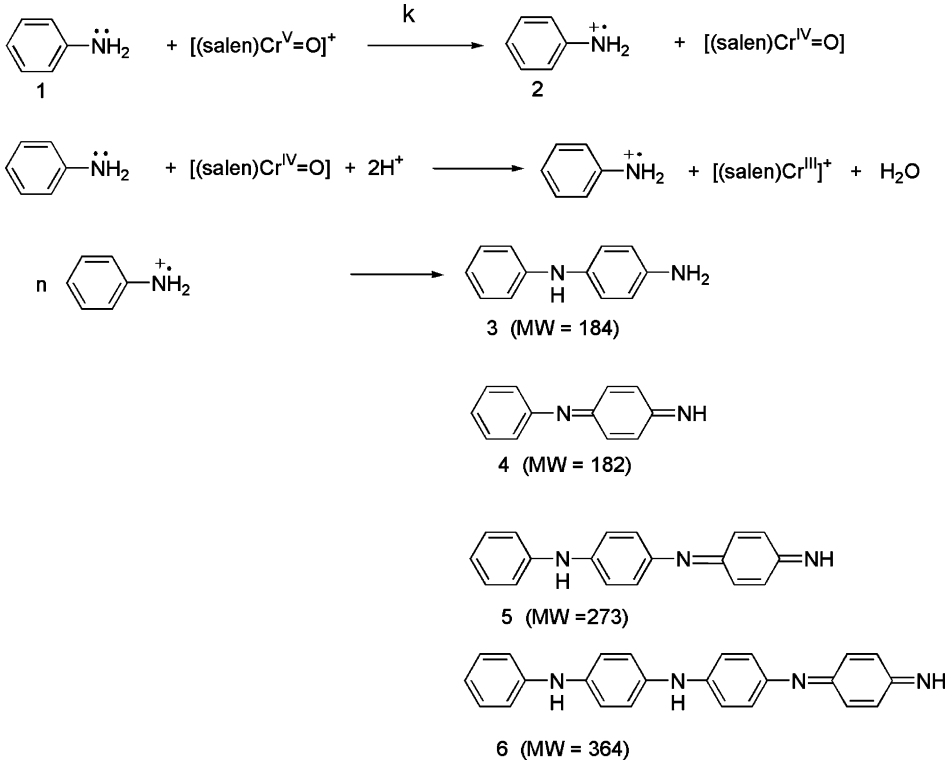
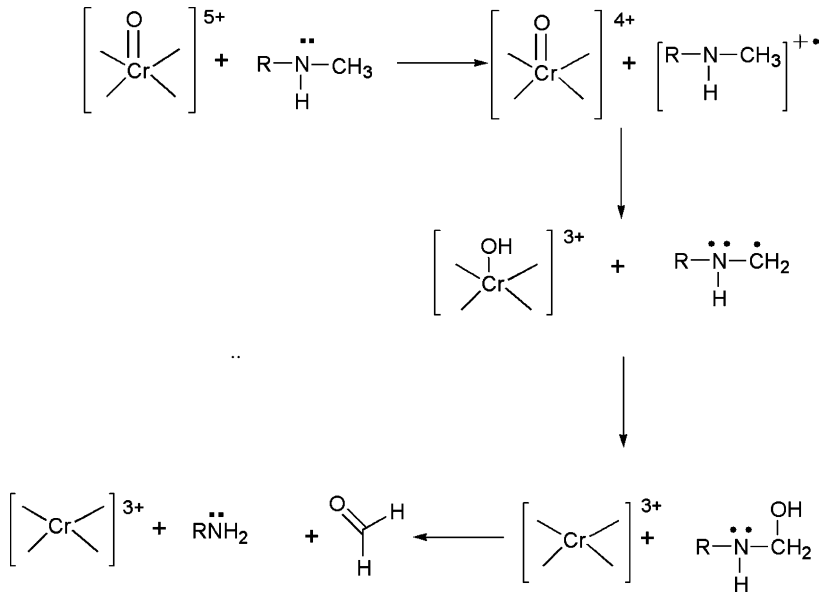


Fig. 9. Spectral changes in the oxidation of *m*-toluidine with oxo(salen)chromium(V). Inset: change in absorbance with time at 560 and 730 nm.



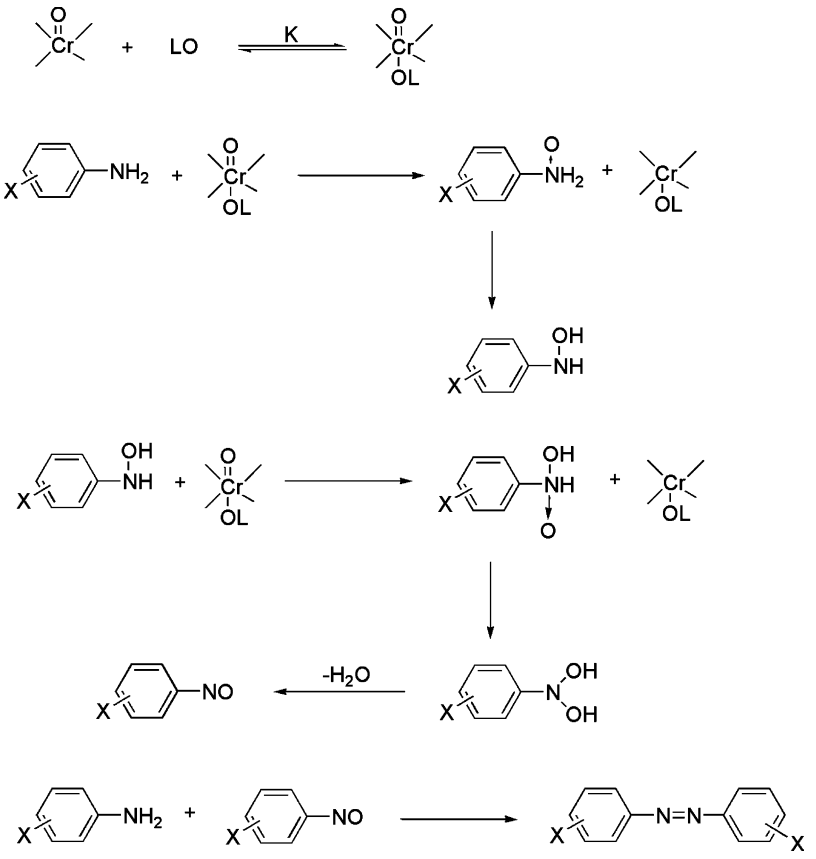
Scheme 8. Formation of oligomers in oxo(salen)chromium(V) ion oxidation of anilines in acetonitrile.



Scheme 9. Demethylation reaction mechanism of secondary amines catalysed by oxo(salen)chromium(V) ion.

The spectral changes (Fig. 9) are consistent with clean conversion of Cr(V) to Cr(III) with an isosbestic point at 518 nm and additional peaks at 470 and 730 nm.

These peaks indicate the formation of oligomers of anilines as the major products of the reaction. To corroborate this, the progress of the reaction has been followed by ES-IMS technique. The electrospray ionization mass spectra of the reaction mixture, prepared using **VIIIa** as the oxidant, and aniline as the substrate were recorded by direct infusion of the reaction mixture at definite intervals of time (1, 10, 30



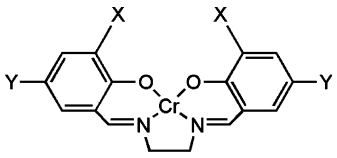
Scheme 10. Mechanism for oxo(salen)chromium(V) ion oxidation of anilines in the presence of ligand oxides.

and 60 min). This study shows that the species with *m*/*z* values 183, 274 and 365 are formed during the course of the reaction, corresponding to the dimer, trimer and tetramer of aniline, respectively. To account for these spectral observations, a mechanism for the oligomerization of aniline (Scheme 8), similar to the electrochemical oxidation is proposed.

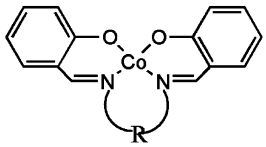
Similar ET reaction leading to oligomerization and dealkylation reaction takes place when oxo(salen) chromium(V) ion reacts with secondary and tertiary amines. For the demethylation reaction, the mechanism shown in Scheme 9 has been proposed.

Contrary to their ET reactions, when the reaction between oxo(salen)chromium(V) ion and aromatic amines is carried out in the presence of donor ligands like pyridine *N*-oxide, triphenylphosphine oxide, oxygenation reaction takes place leading to the formation of corresponding *N*-oxides. To account for this, a mechanism shown in Scheme 10 has been proposed.

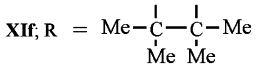
As far as we know, this seems to be the first report regarding the change of course of reaction on the metal–salen catalysed oxidation when the reaction is carried out in the presence of ligand oxides. To get more details on this reaction, product distribution work is in progress.



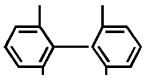
XIa; X = Y = H
XIb; X = H, Y = *t*-Bu
XIc; X = *t*-Bu, Y = H
(a) **XId**; X = *t*-Bu, Y = OMe



XIe; R =



XIf; R =



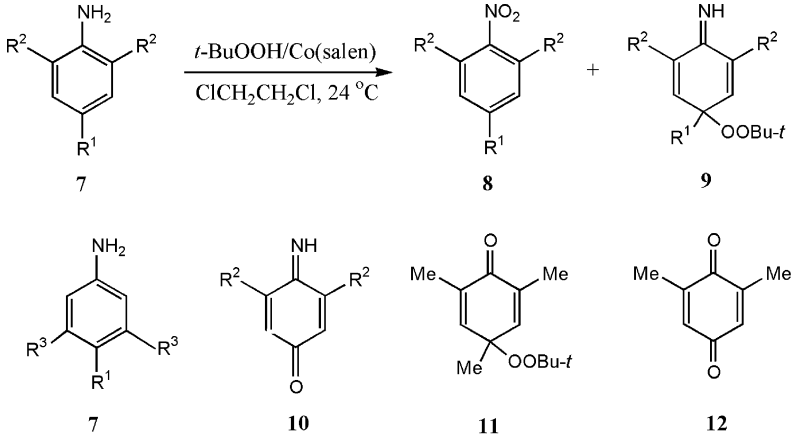
XIg; R =

(b)

Fig. 10. (a and b) Cobalt–salen complexes.

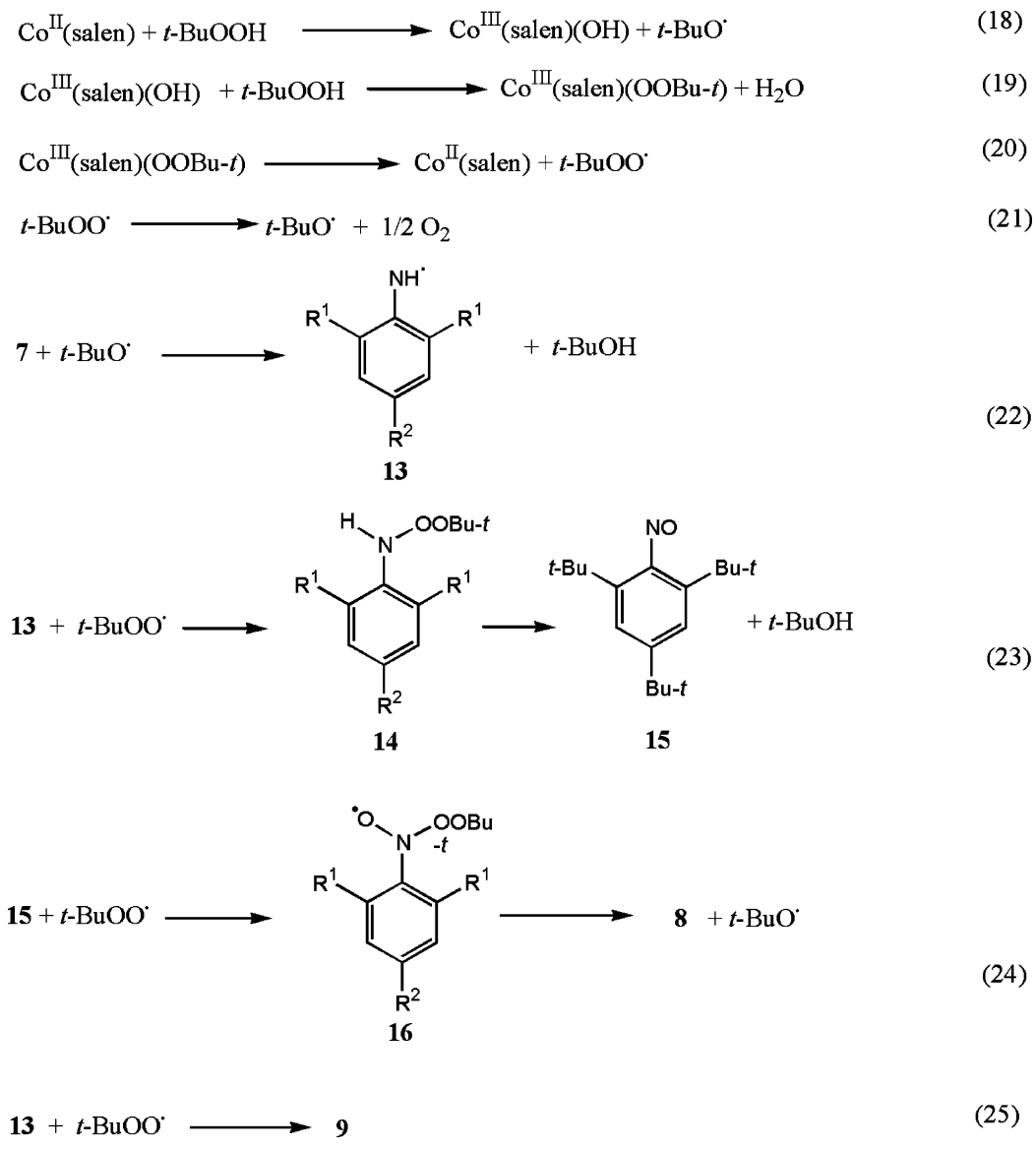
5.2. Cobalt

Co(II)–salen complexes (**XIi–h**) (Fig. 10) catalyse the oxidation of anilines with *tert*-butyl hydroperoxide to give nitrobenzenes (**8**) and 4-(*tert*-butylperoxy)-2,5-cyclohexadien-1-imine derivatives (**9**) in yield distributions depending on the substitution mode of the substrate (Eq. (17)) [107]. 4-Alkyl- and 4-aryl-2,6-di-*tert*-butylanilines gave mixtures of **8** and **9**, where the higher the bulkiness of the 4-substitiuent, the higher the yield of **8**. With 2,4,6-trimethylaniline, the ratio of the nitrogen and C-4 atoms was almost the same: but a hydrolysed product **11** of the imine is obtained.



R_1, R_2 and R_3 = alkyl (17)

2,4,6-Riphenylaniline gave only **8**. Nitrobenzene derivatives are also obtained from 2,6-dialkylanilines and 4-substituted anilines. The catalytic activity of Co(II)–salen ion depends on the nature of the salen ligand [108]. Kinetic studies showed that the rate-determining step may involve hydrogen abstraction from aniline moiety, presumably by *tert*-butoxy radical generated from homolytic decomposition of initially formed Co^{III}(salen)(OOt-Bu). A precursor of **8** is found to be the nitrosobenzene derivative (Scheme 11).



Scheme 11. Mechanism for cobalt–salen catalysed oxidation of anilines in the presence of *tert*-butyl hydroperoxide as proposed by Rieker and co-workers [107].

5.3. Manganese

Goti and co-workers [109] have reported the oxidation of *N*,*N*-disubstituted hydroxylamines to nitrones catalysed by Jacobsen catalyst and this reaction occurs cleanly in the presence of H_2O_2, NaOCl or PhIO as the stoichiometric oxidant. *meso*-3,4-*cis*-Isopropylidenedioxy-1-hydroxypyrrolidine gave the corresponding protected 3,4-*cis*-dihydoxypyrroline *N*-oxide in an enantioenriched fashion up to 36% ee.

6. Concluding remarks

From the details presented above, it can be realized that salen ligands have served as useful starting points for the development of novel catalyst structures. These examples demonstrate how highly effective catalysts can be identified using a single ligand framework. Though the synthesis of chiral sulfoxides and *N*-oxides is yet to be established in most of the metal–salen complexes, it is important to regard these ligand structures as useful platforms for the discovery of new catalysts and reactions [110].

At this stage, we would like to make the following recommendations on the most suitable catalysts for the oxygenation of organic sulfur and nitrogen compounds. The metal–salen complexes of Mn and Cr catalyse the oxidation of organic sulfides to sulfoxides selectively and efficiently by an oxygen atom transfer mechanism. Regarding the role of ligand oxides, Cr–salen complexes need special mention because the reactivity of oxo(salen)chromium(V) ion is largely affected by ligand oxides. For the synthesis of N-oxides from

the aromatic amines, the oxo(salen)chromium(V) ion in the presence of ligand oxides seems to be the most suitable system.

Acknowledgements

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